SUPPORTING INFORMATION

Perchlorate in The Great Lakes: Isotopic Composition and Origin

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13 pages, 3 tables, and 4 figures.

PERCHLORATE EXTRACTION AND PURIFICATION

Field columns that we used for perchlorate extraction from the Great Lakes water for isotopic analysis are custom made simple constructions. We used commercially available clear PVC pipe for construction of 1 L columns, then we filled them with 1 L Purolite A530E bifunctional strong base anion exchange resin. After extracting perchlorate from large quantities of lake water, the perchlorate-loaded columns were transferred from the lake to the University of Illinois at Chicago in coolers filled with ice and stored in a refrigerator before perchlorate extraction.

In addition to perchlorate the anion exchange resin also adsorbs variety of other compounds such as nitrate, sulfate, a range of organic compounds and sediment particles. A flushing of the anion exchange resin with 4 bed volumes of 4 mol/L hydrochloric acid (HCl) and 2 bed volumes of ethanol removes most of the co-adsorbing compounds leaving behind mostly adsorbed perchlorate on the anion exchange resin. Subsequently adsorbed perchlorate is extracted from the anion exchange resin by using an eluent of tetrachloroferrate, which is prepared as a mixed 1 mol/L ferric chloride ($FeCl_3$) and 4 mol/L hydrochloric acid solution.[1] Tetrachloroferrate is highly effective in desorbing perchlorate from the anion exchange resin. In fact, less than 3 bed volumes of the tetrachloroferrate eluent displaces about 90 % of the adsorbed perchlorate from the Purolite A530E bifunctional strong base anion exchange resin (Figure S1). After the elution the perchlorate-bearing eluent was diluted with deionized water (to convert tetrachloroferrate to cationic Fe species) and Fe was removed by passing the

solution through a glass column filled with 600 mL of Bio-Rad AG50W-X12 cation exchange resin. The perchlorate-bearing eluent is then evaporated on a hot plate until about 25 mL of solution remains with addition of a few milliliters of 30 % H_2O_2 to oxidize organic compounds. The evaporation of this azeotropic mixture (~6 M HCl) removes most of the hydrochloric acid without producing any precipitates. Ion chromatography analysis was conducted at this step in order to determine the amount of perchlorate recovered from the sample column. To farther purify perchlorate and to remove the residual impurities (e.g. nitrate) the solution was neutralized to a pH of just above 1 using 10 mol/L NaOH, and reloaded onto 2 mL of Purolite resin for a repeat of the elution and Fe-removal steps described above. Then the final eluent was evaporated down to ~0.5 mL to remove HCl, and the remaining dissolved Cl^- was subsequently removed by diluting the ~0.5 mL solution with 3 mL deionized water and passing through Ag-treated On-Guard columns for Cl^- removal and Ba-treated cation-exchange columns for SO_4^{2-} removal. The solution was then passed through solid-phase extraction (SPE) columns for removal of organics, and finally mixed with excess CsOH to precipitate $CsClO_4$.

Final purification of perchlorate samples was conducted by precipitation and recrystallization of tetra-n-pentylammonium perchlorate ($TPAClO_4$). Perchlorate was precipitated as $TPAClO_4$ in a 5-mL glass vial by adding 1 mL of 0.1 mol/L TPABr (about 30 mg TPA^+) per mg ClO_4^- and allowing at least one hour for the reaction to proceed. Solids were removed by centrifugation and rinsed with 3 x 1 mL of cold deionized water to remove excess TPABr. Washed

$TPAClO_4$ solids were dissolved with 3 x 1 mL of acetone, transferred to a new glass vial and placed in an oven at 50°C overnight to evaporate all acetone to dryness. $TPAClO_4$ was re-dissolved in 200 µL of acetone, and 1 mL of cold deionized water was added to re-precipitate $TPAClO_4$. The vial was placed in the oven at 85°C to evaporate to about 0.5 mL. The vial was then transferred into a refrigerator for at least 30 minutes. Finally, solids were washed with 3 x 1 mL of cold deionized water and then dissolved in 3 x 1 mL of acetone and re-precipitated by evaporation. The purity of $TPAClO_4$ was checked by an ion chromatography.

Conversion from $TPAClO_4$ to $KClO_4$. $TPAClO_4$ was converted to $KClO_4$ for ^{17}O and ^{36}Cl analysis. Freshly prepared 0.5 mol/L KOH in absolute ethanol was used for the conversion of $TPAClO_4$ to $KClO_4$, with K^+/ClO_4^- molar ratio of about 10. $TPAClO_4$ dissolved quickly and $KClO_4$ solids started to precipitate when 0.5 mol/L KOH in absolute ethanol was added to $TPAClO_4$. After one hour, $KClO_4$ solids were separated by centrifugation, rinsed with absolute ethanol, and evaporated to dryness at room temperature. Dry $KClO_4$ solids were dissolved with 3 x 1 mL of deionized water, and analyzed by an ion chromatography to determine yield and purity. The $KClO_4$ solutions were transferred into pre-combusted, labeled Pyrex tubes by Eppendorf pipette and evaporated to dryness. The dry perchlorate samples were sealed under vacuum for decomposition to $KCl + 2O_2$ at 600^{o}C for 30 minutes.

Table S1. Perchlorate concentrations in the water samples from the Great Lakes.

Lake	Date	Station	Depth (m)	ClO_4^- (µg/L)	Mean ClO_4^- (µg/L)
Superior	August, 2008	SU01M	1.5	0.06	
	August, 2008	SU01M	5.1	0.05	
	August, 2008	SU01M	10.5	0.05	
	August, 2008	SU01M	13.1	0.06	
	August, 2008	SU01M	18.8	0.05	
	August, 2008	SU01M	33	0.07	
	August, 2008	SU01M	40.2	0.06	
	August, 2008	SU01M	50.1	0.06	
	August, 2008	SU01M	84.1	0.07	
	August, 2008	SU01M	92.6	0.06	
	August, 2008	SU08M	1.6	0.06	
	August, 2008	SU08M	10	0.05	
	August, 2008	SU08M	16.1	0.05	
	August, 2008	SU08M	35	0.06	
	August, 2008	SU08M	39.9	0.06	
	August, 2008	SU08M	50	0.05	
	August, 2008	SU08M	99.9	0.06	
	August, 2008	SU08M	200	0.05	
	August, 2008	SU08M	280.4	0.07	
	August, 2008	SU08M	288.5	0.05	0.06 ± 0.01
Michigan	August, 2007	MI18M	1.6	0.11	
	August, 2007	MI18M	8.3	0.09	
	August, 2007	MI18M	20.5	0.10	
	August, 2007	MI18M	35.1	0.10	
	August, 2007	MI18M	40.3	0.11	
	August, 2007	MI18M	50	0.10	

	August, 2007	MI18M	100	0.12	
	August, 2007	MI18M	147.9	0.10	
	August, 2007	MI18M	156	0.11	
	August, 2007	MI27M INT	0	0.10	
	August, 2007	MI11 INT	0	0.09	
	August, 2007	MI17 INT	0	0.10	
	August, 2007	MI23 INT	0	0.10	
	August, 2007	MI19 SURF	Surface	0.10	
	August, 2007	MI17 SURF	Surface	0.10	
	August, 2007	MI32 SURF	Surface	0.10	
	August, 2007	MI34 SURF	Surface	0.10	
	August, 2008	MI18M	Sea Chest[a]	0.11	
	August, 2008	MI27M	Sea Chest	0.12	
	August, 2008	MI41M	Sea Chest	0.13	0.10 ± 0.01
Huron	August, 2007	HU15M	1.7	0.10	
	August, 2007	HU15M	6.1	0.10	
	August, 2007	HU15M	12	0.10	
	August, 2007	HU15M	20.4	0.10	
	August, 2007	HU15M	34.2	0.10	
	August, 2007	HU15M	42	0.10	
	August, 2007	HU15M	50	0.12	
	August, 2007	HU15M	56.4	0.10	
	August, 2007	HU32 INT	0	0.13	
	August, 2007	HU37 INT	0	0.11	
	August, 2007	HU53 INT	0	0.12	
	August, 2007	HU38 SURF	Surface	0.11	
	August, 2007	HU48 SURF	Surface	0.10	
	August, 2007	HU37 SURF	Surface	0.11	

	August, 2007	HU53 SURF	Surface	0.10	
	August, 2007	HU61 SURF	Surface	0.10	
	August, 2008	HU15M	Sea Chest	0.12	
	August, 2008	HU45M	Sea Chest	0.12	0.11 ± 0.01
Erie	August, 2008	ER78M	0	0.10	
	August, 2008	ER78M	2.5	0.08	
	August, 2008	ER78M	10.4	0.08	
	August, 2008	ER78M	11.4	0.08	
	August, 2008	ER78M	14	0.08	
	August, 2008	ER78M	16.4	0.08	
	August, 2008	ER78M	21.4	0.08	0.08 ± 0.01
Ontario	August, 2008	ON33M	1.5	0.09	
	August, 2008	ON33M	5	0.09	
	August, 2008	ON33M	12.7	0.09	
	August, 2008	ON33M	40.1	0.09	
	August, 2008	ON33M	50.1	0.09	
	August, 2008	ON33M	99.9	0.09	
	August, 2008	ON33M	127	0.10	
	August, 2008	ON33M	135.8	0.09	0.09 ± 0.01

[a] The “sea chest” is a port through the ship’s hull about one meter below water level. Water was pumped continuously through this port up to the laboratory for sampling of perchlorate on 1-liter ion-exchange resin columns for isotopic analysis.

Table S2. Physical parameters of the Great Lakes.[2-4]

Lakes	Residence time (year)	Lake volume (km^3)	Surface area (km^2)	Drainage area (km^2)	Over Lake Evaporation (km^3/year)	Over Lake Precipitation (km^3/year)	Over Land Precipitation (km^3/year)
Superior	179.8	12,115	81,925	128,084	50	65	104
Michigan	110.2	4,947	57,291	115,804	38	47	96
Huron	21.3	3,567	59,560	132,208	39	51	117
Erie	2.7	499	25,404	60,602	24	24	56
Ontario	7.5	1,651	19,121	65,118	13	17	62

Table S3. Perchlorate mass-balance model results. Units are tonnes/year, except total ClO_4^- in tonnes.

Lakes	Atmospheric ClO_4^- Input	Upstream ClO_4^- Inflow	Total ClO_4^- Input	ClO_4^- Outflow	ClO_4^- [Input–Ouflow]	Total ClO_4^- (tonne)
Superior	4.8 ± 4.6	n.a.	4.8 ± 4.6	4.2	0.6 ± 4.6	727
Michigan	4.0 ± 3.9	n.a.	4.0 ± 3.9	4.5	-0.5 ± 3.9	495
Huron	4.7 ± 4.5	8.4	13.1 ± 4.5	18.6	-5.5 ± 4.5	392
Erie	2.3 ± 2.2	19.2	21.5 ± 2.2	15.8	5.7 ± 2.2	40
Ontario	2.2 ± 2.1	15.8	18.0 ± 2.1	20.7	-2.7 ± 2.1	149

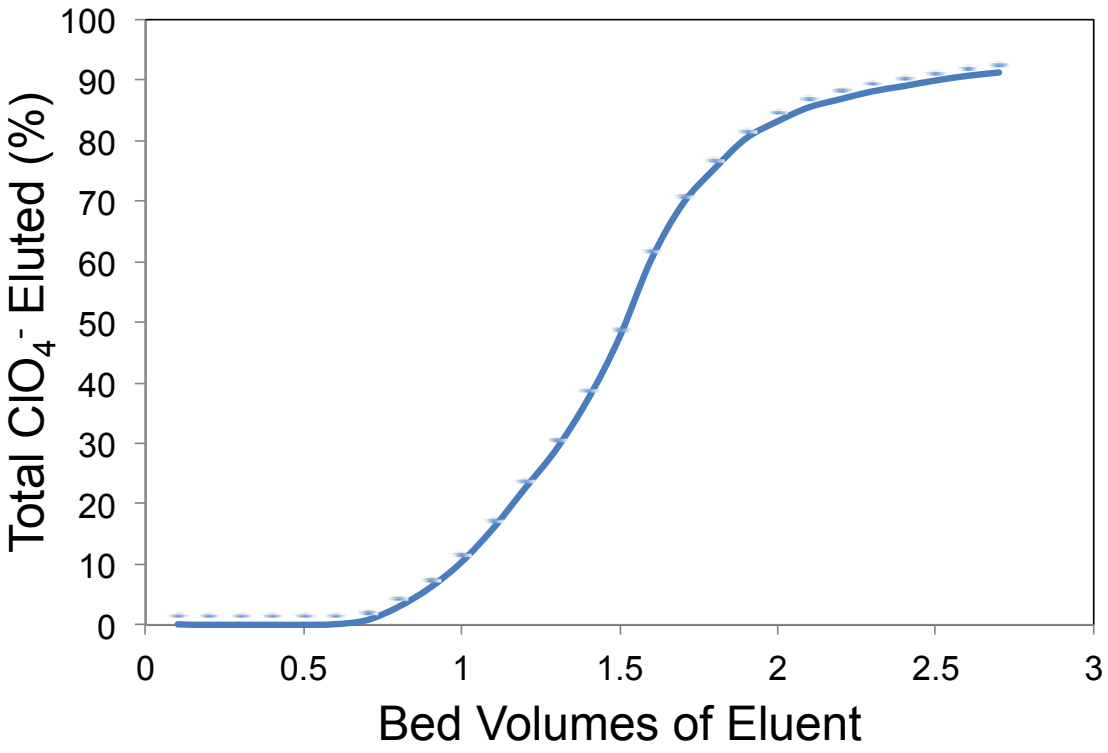

Figure S1. Diagram demonstrating the efficiency of perchlorate elution by tetrachloroferrate eluent.

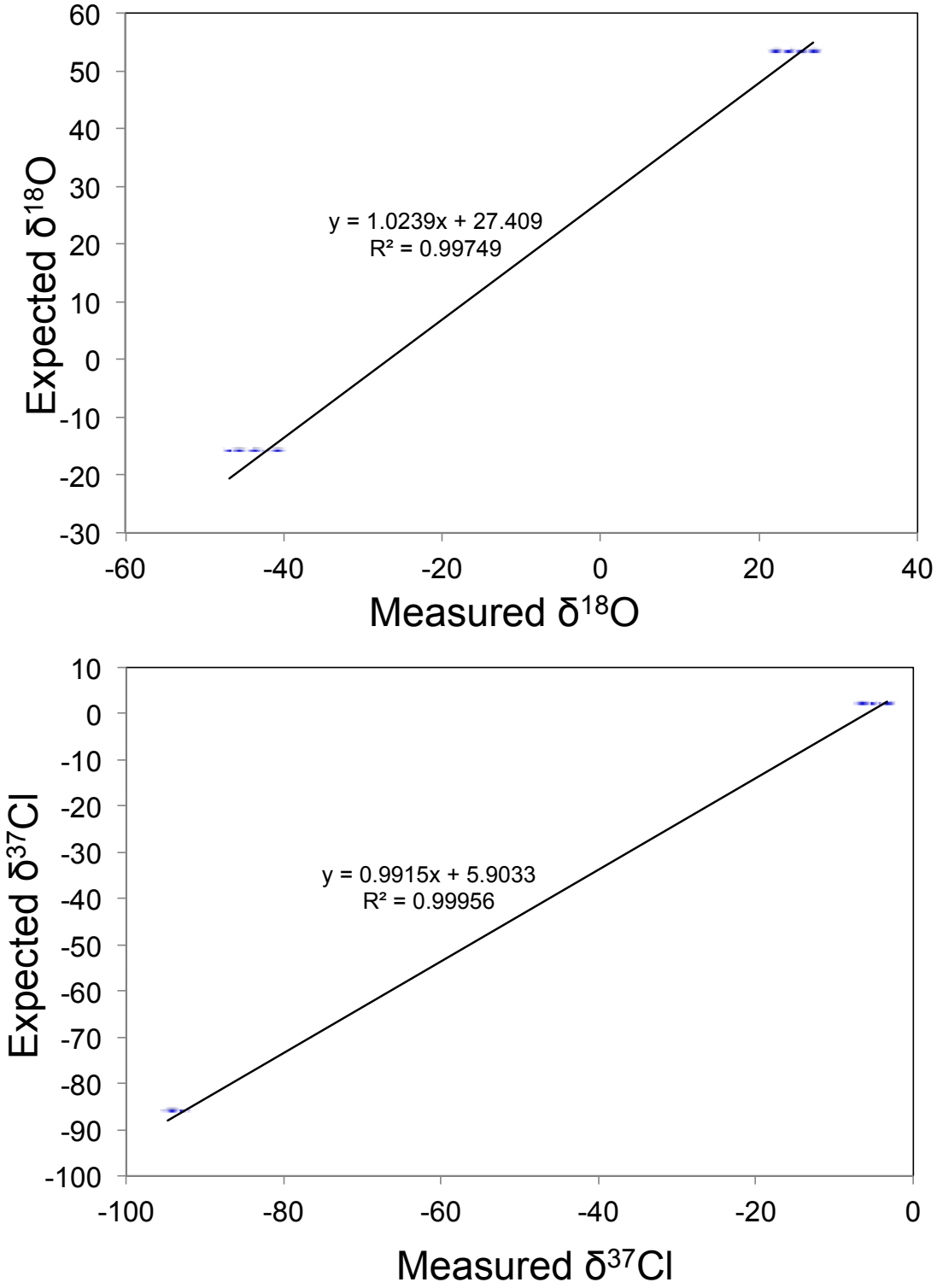

Figure S2. SIMS calibration curves for the $\delta^{18}O$ (upper diagram) and $\delta^{37}Cl$ (lower diagram) values of $KClO_4$ isotopic reference materials USGS-37 and USGS-38.

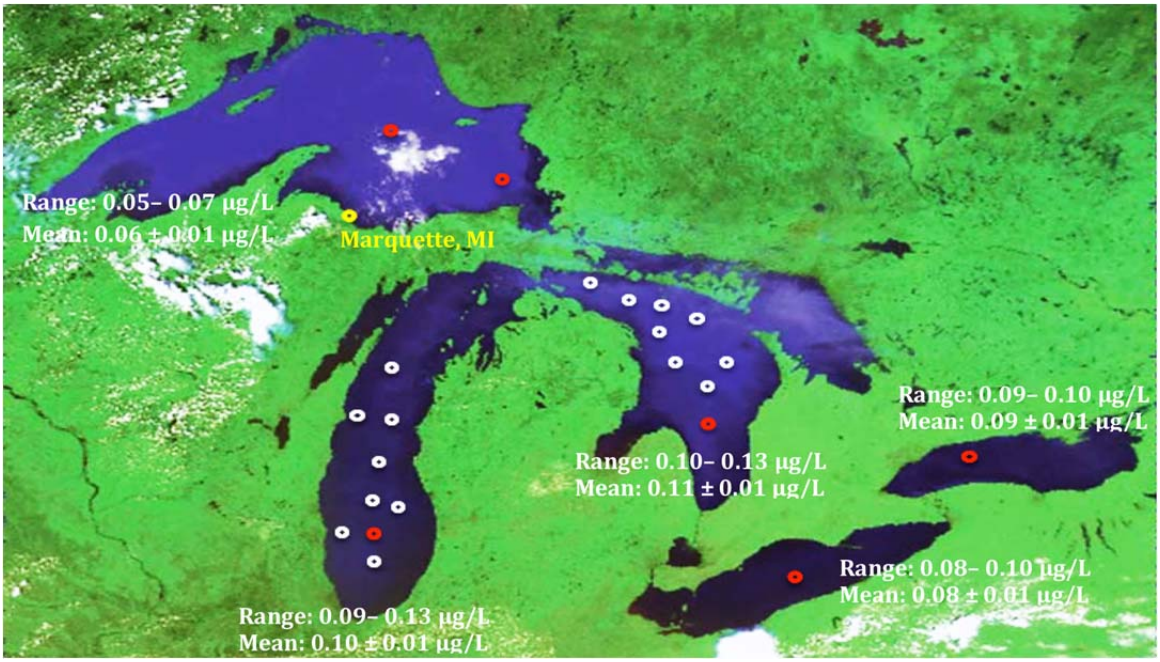

Figure S3. Locations of the water samples collected from the Great Lakes for perchlorate concentration analysis. Map also shows the range and the mean values of the observed perchlorate concentrations for all samples. Red symbols show the location of the perchlorate concentration depth profiles, whereas Marquette, MI (yellow symbol) is the location of the Lake Superior perchlorate samples for isotopic analysis. The Great Lakes map is from NOAA, Great Lakes Environmental Research Laboratory.[5]

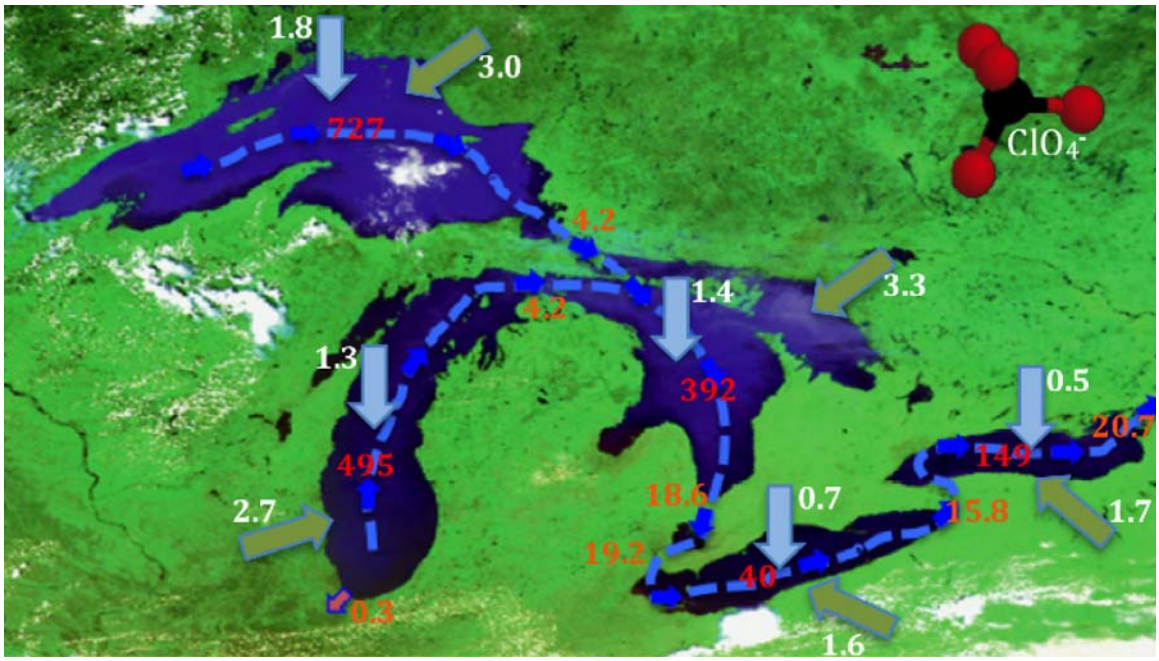

Figure S4. Estimated perchlorate fluxes in the Great Lakes. Red numbers represent total perchlorate inventories in each lake (tonne), white numbers next to the arrows represent perchlorate fluxes (tonne/year) from direct atmospheric deposition and from the drainage basins when assuming 14.1 ng/L perchlorate concentration in the rainwater and equal dry and wet depositions, and orange numbers represent perchlorate outflows from the lakes (tonne/year). The Great Lakes map is from NOAA, Great Lakes Environmental Research Laboratory.[5]

References

(1) Gu, B.; Brown, G. M.; Maya, L.; Lance, M. J.; Moyer, B. A. Regeneration of Perchlorate (ClO_4^-)-Loaded Anion Exchange Resins by a Novel Tetrachloroferrate ($FeCl_4^-$) Displacement Technique. *Environ. Sci. Technol.* **2001,** *35* (16), 3363-3368.

(2) Chapra, S. C.; Dove, A.; Rockwell, D. C. Great Lakes Chloride Trends: Long-Term Mass Balance and Loading Analysis. *J. Great Lakes Res.* **2009,** *35* (2), 272-284.

(3) Quinn, F. H. Hydraulic residence times for the Laurentian Great Lakes. *J. Great Lakes Res.* **1992,** *18* (1), 22-28.

(4) GLERL Great Lakes Monthly Hydrologic Data. http://www.glerl.noaa.gov/data/arc/hydro/mnth-hydro.html **2012**, Ann Arbor, MI.

(5) NOAA/GLERL NOAA, Great Lakes Environmental Research Laboratory satellite imagery. http://www.glerl.noaa.gov **2014**, Ann Arbor, MI.